A FURTHER INVESTIGATION

OF THE

CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE

JOHNS HOPKINS UNIVERSITY FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY.

BY

SOL. REID McKEE.

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This investigation was suggested by Professor Ira Remsen, and the work carried on under his supervision. It gives the author pleasure to make this acknowledgment to him for the assistance which he has so generously given. Further, the author takes this opportunity to express his appreciation of the instruction and inspiration which he has received both from Professor Remsen and Professor Morse.

I. Introduction.

In studying the action of phosphorus pentachloride on salts of orthosulphobenzoic acid Remsen and Dohme[1], in 1889, obtained a substance which had the composition $C_7H_4SO_3Cl_2$, but nothing in their work indicated that the substance was not an individual. The constitution given to the substance was $C_6H_4\begin{cases}COCl\\SO_2Cl,\end{cases}$ the principle support for this being the formation of chloro-ethers of the constitution,

$$C_6H_4\begin{cases}CO.OC_2H_5\\SO_2Cl\end{cases}.$$

From this ether and from the original chloride, by boiling with absolute alcohol, an acid ether, of structure $C_6H_4\begin{cases}CO.OC_2H_5\\SO_2OH\end{cases}$, was obtained, indicating a difference in the two chlorine atoms.

Remsen and Coates,[2] in 1891, obtained the first evidence that the chloride above mentioned was not an individual; for by the action of aniline on it they obtained two isomeric anilides and an anil.

In the following year Remsen and Kohler[3] further studied the action of aniline on this substance, and confirmed the work of Coates. One of the anilides melted at 196° and behaved in all respects as a normal acid anilide, while the other melted at about 270°, with decomposition, and had a different behavior. The first was called the fusible anilide and the second the infusible. They succeeded in getting some crystals of one of the chlorides in pure condition (melting-point 76°) and showed that only the fusible anilide was formed when this was used in the reaction; or, under different conditions, the anil. From the mixed chlorides, however, they got both fusible and infusible anilides. Further, they succeeded in effecting a synthesis of the fusible anilide, starting with toluenesulphone chloride.

$$C_6H_4\begin{cases}CH_3\\SO_2Cl\end{cases}.$$

[1] Am. Chem. J., **11**, 332. [2] Am. Chem. J., **17**, 311.
[3] Am. chem. J., **17**, 330.

Both the conduct and the method of synthesis argue for

$$C_6H_4\begin{cases}CO.NHC_6H_5\\SO_2.NHC_6H_5\end{cases}$$

as the structure of the fusible anilide, and hence for

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}$$

as the structure of the high-melting[1] chloride.

The other chloride they were unable to get in pure condition, but only as an oily mass containing some of the high-melting constituent. The purest of this low-melting chloride obtainable gave, with aniline, mostly the infusible anilide; and the amount of the infusible anilide seemed to increase as more of the high-melting chloride was removed. The most probable structure for the infusible anilide was

$$C_6H_4\begin{cases}C(NHC_6H_5)_2\\SO_2\end{cases}O,$$

and for the low-melting chloride

$$C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}O.$$

The next year Remsen and A. P. Saunders[2] studied the action of ammonia, phenol, and benzene and aluminium chloride on the chlorides. Now, for the first time, the high-melting chloride was available, in quantities, in pure condition. They also succeeded in getting a small quantity of the low-melting chloride pure (melting-point 21.5°–22.5°) by fractional crystallization from petroleum ether.

By the action of phenol on the pure high-melting chloride and on the mixed chlorides they obtained a normal diphenyl ether, to which the structure $C_6H_4\begin{cases}CO.OC_6H_5\\SO_2.OC_6H_5\end{cases}$ was given. Another, red-colored, substance was obtained in this reaction, but was not investigated.

By the action of benzene and aluminium chloride on the pure high-melting and mixed chlorides, at ordinary tempera-

[1] The chlorides will be distinguished by the names high-melting and low-melting, instead of solid and liquid, as heretofore.

[2] Am. chem. J., 17, 347.

tures, they obtained a substance of structure $C_6H_4\begin{cases}CO.C_6H_5\\SO_2Cl\end{cases}$, orthobenzoylbenzenesulphone chloride. When this substance, or the pure high-melting, or mixed chlorides was acted upon by benzene and aluminium chloride, and heat applied, the action went to the full extent, both of the chlorine atoms being replaced, and orthobezoyldiphenylsulphone,

$$C_6H_4\begin{cases}CO.C_6H_5\\SO_2.C_6H_5\end{cases},$$

formed. The formation of the intermediate product, mentioned above, argues for the symmetrical formula,

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases},$$

as the structure of the high-melting chloride.

From the low-melting chloride, by the action of benzene and aluminium chloride, no satisfactory results were obtained.

At the suggestion of Professor Remsen a further investigation of these two chlorides was undertaken, the results of which are recorded in this paper.

II. Preparation of Materials.

The starting-point in the preparation of the chlorides is commercial saccharin, and from this the acid potassium salt of orthosulphobenzoic acid was prepared by the method described by Remsen and Saunders.[1] In the preparation of the chlorides from the salt some changes have been made, and hence the details of this process are given. The yield by the method formerly used was not as large as was desirable, being only 65–70 per cent. of the calculated. Mr. Karslake, of this laboratory, in working on a derivative of the low-melting chloride, observed that when he increased the amount of phosphorus pentachloride the yield of this derivative was larger.

A few experiments of my own, bearing on this point, showed that $2\frac{1}{2}$ molecules of phosphorus pentachloride was only a slight excess, and that the yield was about 95 per cent

[1] *Loc. cit.*

of the calculated. The process is as follows: The acid potassium salt, as quantities of 75–100 grams, is placed in a porcelain dish with $2\frac{1}{2}$ molecules phosphorus pentachloride, and rubbed with a pestle until the action is over, when the whole mass has become liquid. This liquid mass is then transferred to a flask, and the phosphorus oxychloride distilled off under diminished pressure. In this operation a small quantity of phosphorus pentachloride collects in the tube, showing that it is present in slight excess. The oxychloride may be evaporated off, as in the former method, by heating the dish on a water-bath for about three hours, if it is preferred, as the yield was practically the same in both cases. When the oxychloride is driven off the mass is transferred to a tall glass cylinder, containing 200–250 cc. of water, and washed by vigorously churning it with a glass rod terminating in a ring. After two or three washings it is poured into a beaker, and placed in a freezing mixture, when it soon becomes completely solid. To prevent the formation of a solid cake and also to facilitate the freezing, it should be stirred and broken up with a spatula. It is then thoroughly ground up in a mortar with ice-water, transferred to a filter, and washed with ice-water, with the aid of a pump. In this way the chlorides can be freed from potassium chloride and phosphorus compounds. After sucking dry with the pump, the mass can be further dried by placing it between two pieces of drying paper and pressing with a plate, or rolling a glass rod over it. Care must be taken, however, not to touch it with the hands, or anything that is warm. If the mass is now placed in a beaker and kept in a desiccator over calcium chloride, in a cool place, it remains a dry solid, and can be handled very easily. The wash-water should be evaporated, so as to recover any little of the acid potassium salt it may contain.

Several experiments were made to see if the chlorides could, with advantage, be extracted with ether, after distilling off the phosphorus oxychloride, but no distinct advantage was gained. In two cases, however, when 2 molecules of phosphorus pentachloride was used and the chlorides extracted with ether, crystals of another substance were de-

posited in small quantity from the ether extract, before the chlorides separated. These were thought to be the anhydride of orthosulphobenzoic acid, $C_6H_4\begin{cases}CO\\SO_2\end{cases}O$, and an investigation by Mr. Sohon, of this laboratory, has proved that the assumption was correct, and that the substance is formed in large amount when a smaller quantity of phosphorus pentachloride is used.

III. Separation of the Two Chlorides.

1. *The Pure High-Melting Chloride.*—Heretofore this substance has been obtained according to the method worked out by Mr. J. E. Bucher, of this laboratory, by dissolving the mixed chlorides in chloroform, shaking this solution with ammonia, separating the chloroform solution and evaporating. Ammonia acts much more easily on the low-melting than on the high-melting chloride, and thus it is possible to get rid of the former.

Shaking the mixed chlorides with aqueous ammonia has been tried, and it was found that nearly all the low-metling constituent could be destroyed in this way. By repeating this several times, and then crystalling from ligroin, the high-melting chloride can be prepared in pure condition. This substance melts, according to Remsen and Saunders,[1] at 76°–77° uncorr, but a product has been obtained, by the above method, which melts considerably higher. Especial purification was undertaken to see if a product could be obtained which would not give the red color when heated with phenol. A portion melting at 76°–77° was alternately shaken with dilute ammonia and crystallized from ligroin (boiling-point 90°–125°) nine times. The melting-point gradually rose until the sixth crystallization, when it was 79°–79.5°, uncorr.; but after that there was no further rise. The thermometer used was correct for the boiling-point of water.

Mr. Karslake, of this laboratory, has found that when the mixed chlorides are dissolved in ether, shaken with dilute ammonia, and the ether solution evaporated the high-melting chloride can be obtained very easily.

So that the best method, and the one now used, is to shake

[1] *Loc. cit.*

the mixed chlorides with dilute aqueous ammonia until nearly all the low-melting constituent is destroyed; then dissolve in ether, cool down to about 0° by adding ice, and shake with dilute ammonia. The ether solution is separated, dried over calcium chloride, and most of the ether distilled off. From the residue good crystals of the chloride, melting at 79°–79.5°, are obtained.

2. *The Pure Low-Melting Chloride.*—By fractional crystallization of the mixed chlorides from petroleum ether in the cold, Remsen and Saunders[1] obtained a small quantity of the low-melting chloride in pure condition (melting-point 21.5°–22.5°).

After various attempts to effect a separation of the two chlorides during the past year, a method has been devised which gives satisfactory results, though it is somewhat tedious. It is as follows: A portion of the mixed chlorides is dissolved in absolute ether, placed in a cool place, and allowed to stand for about a day, when nearly all the ether will have evaporated, and there will be a separation of crystals of the high-melting chloride. The oily portion, consisting mainly of the low-melting chloride, is drained off and dissolved in ligroin (boiling-point 90°–125°). This solution is placed in an Erlenmeyer flask and a current of dry air drawn through the flask. The liquid must be kept cold, however, or else the substance will not crystallize; and for this purpose a refrigerating box was devised. This is made of galvanized iron, and consists of two chambers, an outer and an inner, with a space of about four inches between them. The outer chamber has a cover, and is surrounded by a thick layer of cotton. When this is filled with broken ice the temperature can be kept at 0° for several days. The flask, containing the solution, is placed in the inner chamber, and this covered with cotton, or a piece of asbestos board with small holes cut in it for the passage of the glass tubes leading to the flask. The air is dried with sulphuric acid and calcium chloride. After a time two kinds of crystals are noticed, stout columns and radiating tufts of fine needles. The columns melt at 70°–75°, and the needles 22°–23° uncorr. As a rule the columns do not appear until some time after crystallization begins, owing to the fact that part of

[1] *Loc. cit.*

the high-melting chloride has already been removed by crystallization from ether. When evaporation has proceeded far enough, the mother-liquor is poured off, and the columns removed with a properly constructed spatula. If this is done carefully, very little is left except the radiating tufts. These are then redissolved in ligroin, and the process repeated. Sometimes the columns are observed in the second crystallization, if the solution is evaporated low enough; if so, they are removed as before. As a rule the substance was crystallized twice after columns ceased to appear, and all the low-melting chloride used in the experiments, hereafter described, was thus treated. After the final crystallization, the mother-liquor should be washed out with cold ligroin, and the crystals removed and dried. The crystals thus obtained melted at 21.5°–22.5° uncorr., and the melting-point was not lowered by recrystallization. In no case should the solution of the chlorides be saturated, even at 0°, for the solution then becomes cloudy and the substance does not crystallize so well. When the high-melting chloride is removed it is best, in all crystallizations, to add 3 or 4 individual crystals of the low-melting chloride when crystallization is just about to begin, for without this, in some cases, only an oil is obtained.

Petroleum ether of different boiling-points was tried, but nothing gave as satisfactory results as ligroin, boiling-point 90°–125°. Moreover, it was found necessary to purify the commercial ligroin, as the chlorides absorb something from it and become darkened in consequence. It was shaken in a large separating-funnel with strong sulphuric acid until it almost ceased to color the acid, washed with hot water, then with a hot, dilute solution of sodium hydroxide, then with hot water until free from alkali; then dried over calcium chloride and filtered.

IV. Action of Water on the Pure Chlorides.

Remsen and Saunders[1] showed that both of the pure chlorides are decomposed by water, yielding orthosulphobenzoic acid and hydrochloric acid, but noted no difference in the rate of action. The following experiment shows that there is a dif-

[1] *Loc. cit.*

ference, and that the low-melting chloride is acted on by water about three times as rapidly as the high-melting. 0.8 gram of each of the chlorides was placed in a small flask, and 50 cc. of water added. The flasks were shaken and placed aside. Every twenty-four hours 10 cc. of the water was removed and titrated with silver nitrate; and 10 cc. of pure water added. The results were as follows:

Pure high-melting chloride. Decomposition.		Pure low-melting chloride. Decomposition.	
Daily.	Total.	Daily.	Total.
1....3.96	3.96	1....11.87	11.87
2....5.66	9.60	2....21.30	32.20
3....5.48	15.08	3....17.77	50.78
4....4.71	19.80	4....14.08	64.91

V. Action of Phenol.

By heating the high-melting and the mixed chlorides with phenol, Remsen and Saunders[1] obtained a normal diphenyl ether of orthosulphobenzoic acid, $C_6H_4 \begin{cases} CO.OC_6H_5 \\ SO_2.OC_6H_5 \end{cases}$, and a red-colored substance which was not investigated. Their work was repeated, and the diphenyl-ether obtained, but no considerable amount of the red-colored substance, although efforts were made to get it. After the action was over, instead of treating with sodium hydroxide, ammonia was added. The whole mass at once became oily, and, on standing for some time, became solid. From this a new substance was obtained, as will be shown below. The action of phenol was tried at various temperatures, ranging from 40° to 120°, but the temperature at which the largest yields and the cleanest products were obtained was 40°–45°. In every experiment with phenol the red color was observed, even with the purest specimens of the chlorides.

1. *Action on the High-Melting Chloride.*—5 grams of the chloride, (melting-point 79°–79.5°), was heated with 4 grams (2 molecules) phenol for five hours at 40°–45°, and then dilute ammonia added. After stirring for some time the oily mass became solid; it was then filtered, washed and dried. The yield was 4.175 grams. This, when crystallized from alcohol, gave the diphenyl ether and the new substance described below.

[1] *Loc. cit.*

Phenyl Orthosulphamidobenzoate.—When the solid substance, obtained above, was dissolved in alcohol, and water added slowly till crystallization was just about ready to begin, and the solution then allowed to cool slowly, crystals of the diphenyl ether (melting-point 117°–118°) separated. After filtering, the mother-liquor was evaporated and a little more water added, when it became cloudy. On cooling slowly, feathery-shaped crystals separated, which melted at 128°–130°, and on recrystallization melted quite sharply at 131°–132° uncorr. This substance proved to be an amide of the formula $C_6H_4 \begin{cases} CO.OC_6H_5 \\ SO_2NH_2 \end{cases}$, formed by the following reactions:

$$C_6H_4 \begin{cases} COCl \\ SO_2Cl \end{cases} + HOC_6H_5 = C_6H_4 \begin{cases} CO.OC_6H_5 \\ SO_2Cl \end{cases} + HCl;$$

$$C_6H_4 \begin{cases} CO.OC_6H_5 \\ SO_2Cl \end{cases} + NH_3 = C_6H_4 \begin{cases} CO.OC_6H_5 \\ SO_2NH_2 \end{cases} + HCl.$$

The analyses were as follows:

I. 0.1527 gram gave 0.1241 gram $BaSO_4$ (Carius method).
II. 0.1532 " " 0.1251 " " " "
III. 0.314 " " 0.01637 " nitrogen (absolute ").

	Calculated for $C_{13}H_{11}SO_4N$.	Found. I.	II.	III.
S	11.55	11.16	11.22	....
N	5.05	....	....	5.21

The second sulphur determination was made by Mr. Ragland, and the nitrogen determination by Mr. Mackay, of this laboratory.

The intermediate product could not be eliminated. Several attempts were made to get the corresponding acid by boiling with water after the action was over, and also to prepare the anilide, but all of these were unsuccessful; only orthosulphobenzoic acid and the fusible and infusible anilides could be obtained. The presence of the phenol complicated matters very much, and besides, the action of phenol on the original chloride could never be made complete.

At higher temperatures the yield of the phenyl orthosulphamidobenzoate was smaller, though a small quantity was obtained even as high as 100°. It seems, then, very probable that part of the action, at least, gives an intermediate pro-

duct, and that at a higher temperature the action goes to the full extent. The diphenyl ether, however, is formed at the lowest temperature at which action takes place at all; at 40°–45° about equal quantities of each are formed.

2. *Action of the Mixed Chlorides.*—When the mixed chlorides were used, the same two substances were obtained, though there was proportionally a somewhat smaller yield of phenyl-orthosulphamidobenzoate.

3. *Action on the Low-Melting Chloride.*—2 grams of the low-melting chloride was heated with 1.6 grams phenol for five hours, at 40°–45°, and the product treated as above. Both substances were obtained and in approximately equal quantities. It was hoped that an isomeric substance would be formed, but there was not the slightest indication of such.

VI. Decomposition of the Diphenyl Ether.

1. *Decomposition with Ammonia.*—The diphenyl ether is not acted on by strong ammonia under ordinary pressure, even when boiled. When heated in a sealed tube for two hours at the temperature of the water-bath, the action is very slight, but, when heated in a sealed tube at 125° for four hours, the decomposition is complete. There is formed a dark-colored solution, which gives off phenol on heating. By heating with water all the phenol can be driven off, and on evaporating to a small bulk, crystals of a sweet-tasting substance separate. When these are dissolved in water and the solution acidified, there is a large deposit of saccharin. The substance formed is the ammonium salt of saccharin, $C_6H_4\begin{smallmatrix}/CO\\\backslash SO_2\end{smallmatrix}\!\!\rangle N.NH_4$, and the reaction is, in all probability, represented thus:

$$C_6H_4\begin{smallmatrix}/CO.OC_6H_5\\\backslash SO_2.OC_6H_5\end{smallmatrix} + 2NH_3 = C_6H_4\begin{smallmatrix}/CO\\\backslash SO_2\end{smallmatrix}\!\!\rangle N.NH_4 + 2C_6H_5OH.$$

2. *Decomposition with Hydrochloric Acid.*—Portions of the diphenyl ether were heated with concentrated hydrochloric acid, in a sealed tube, at 100°, at 125°, and at 150° for several hours without action. When, however, it was heated at 200° for six hours, there was complete decomposition The dark-colored liquid, when evaporated, gave a strong odor of phenol, and

when the phenol was all driven off, the solution was evaporated to dryness to expel the hydrochloric acid. The solid residue, when dissolved in water, gave a strong acid reaction. This was neutralized with barium carbonate, boiled with animal charcoal, and evaporated. Good crystals were obtained, answering to the description of the neutral barium salt of orthosulphobenzoic acid, made and described by Remsen and Dohme.[1]

The reaction may be expressed thus:

$$C_6H_4\begin{cases}CO.OC_6H_5\\SO_2.OC_6H_5\end{cases} + 2H_2O = C_6H_4\begin{cases}COOH\\SO_2OH\end{cases} + 2C_6H_5OH.$$

I. 0.3394 gram when heated lost 0.0328 gram water.

II. 0.3394 gram gave 0.212 gram $BaSO_4$.

	Calculated for $C_7H_4SO_5Ba + 2H_2O$.	Found.
H_2O	9.65	9.66
Ba	36.72	36.74

3. *Decomposition with Potassium Hydroxide.*—A portion of the diphenyl ether was heated for some time on a water-bath with a moderately concentrated solution of potassium hydroxide, but as there seemed to be no action, it was boiled for about twenty minutes. Still there was no action, as was shown by filtering and evaporating the filtrate. When treated with alcoholic potash, however, and heated, the whole went into solution, and almost immediately there was a deposit of fine needles. The odor of phenol was also very pronounced, when the filtrate was acidified. The substance was recrystallized from alcohol and analyzed. In appearance the crystals corresponded to the neutral potassium salt of orthosulphobenzoic acid, made and described by Remsen and Dohme.[2] The reaction may be represented thus:

$$C_6H_4\begin{cases}CO.OC_6H_5\\SO_2.OC_6H_5\end{cases} + 2KOH = C_6H_4\begin{cases}COOK\\SO_2OK\end{cases} + 2C_6H_5OH.$$

I. 0.220 gram heated at 185° lost in weight 0.0181 gram.

II. 0.220 gram gave 0.1255 gram K_2SO_4.

[1] *Loc. cit.* [2] *Loc. cit.*

	Calculated for $C_7H_4SO_5K_2 + 1\frac{1}{2}H_2O$.	Found.
H_2O	8.85	8.22
K	25.57	25.54

VII. Action of Resorcin.

1. *Action on the High-Melting Chloride.*—A portion of the pure high-melting chloride was heated with resorcin (2 molecules) for four hours, at 75°–80°, the action taking place very readily at that temperature. The whole mass became very soft and hydrochloric acid was given off freely. At the end of this time it had become very stiff. The temperature was then raised to 90°, and the heating continued about two hours longer. The evolution of hydrochloric acid had about ceased, and the mass had become quite hard. On adding sodium hydroxide, the whole went into solution. This solution was very dark-colored, but, on diluting, it gave a beautiful fluoresence, and on adding acid, a yellowish-brown mass was precipitated. This was redissolved, heated with animal charcoal, filtered and precipitated by acid, when the color had become brownish yellow. It was dried in the air on a plate, and then in a desiccator.

A portion was heated at 125°–130° for three hours, but lost no water, as the fluoresceïns usually do.

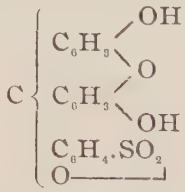
I. 0.1467 gram gave 0.329 gram CO_2 and 0.0498 gram H_2O.
II. 0.1509 " " 0.338 " " " 0.0506 " "
III. 0.1553 " " 0.0948 " $BaSO_4$ (Carius method).

	Calculated for $C_{19}H_{12}O_8S$.	Found. I.	II.	III.
C	61.9	61.2	61.1	....
H	3.26	3.76	3.72	....
S	8.69	....	....	8.39

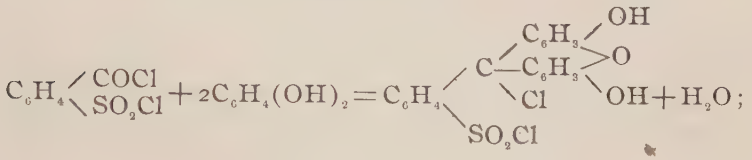
The combustions were made by the lead chromate method as modified by DeRoode,[1] but it was found necessary to mix the substance with potassium bichromate in a boat, to burn it. This substance is a sulphon fluoresceïn, but does not seem to be identical with that prepared by Remsen and Linn[2], and Remsen and Blackshear[3] from dioxybenzoylbenzenesulphonic acid, the difference being 1 molecule of water.

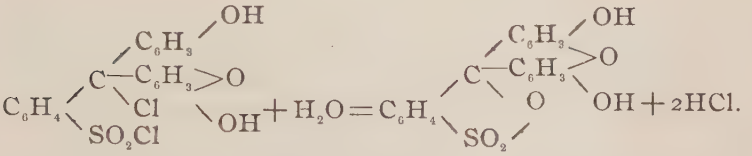
[1] Am. Chem. J. **12**, 226. [2] Am. Chem. J. **11**, 73.
[3] Am. Chem. J. **14**, 455.

Analogous to the fluoresceïns the formula would be written thus:



The formation of this substance from the symmetrical chloride can be accounted for in this way:





2. *Action on the Low-melting Chloride.*—When the low-melting chloride was heated with resorcin, at the same temperature, reaction took place in the same way, and when sodium hydroxide was added the whole mass went into solution, just as before, and gave a fluorescent substance. This was precipitated by acids, and acted in every way just as the substance above described, and is in all probability the same substance.

VIII. Action of Aniline.

1. *Action on the High-Melting Chloride*—Remsen and Kohler[1] showed that when the high-melting chloride is treated with aniline only the fusible anilide is obtained. Their work was repeated and confirmed, there being no evidence of any other substance.

2. *Action on the Low-Melting Chloride.*—In accordance with

[1] *Loc. cit.*

work of Remsen and Kohler, it was expected that the action of aniline on the pure low-melting chloride would give only the infusible anilide, but the results were different. 0.8 gram of the chloride was dissolved in ether in a small flask, and a dilute ether solution of aniline added slowly, the flask being kept in cold water. Action took place at once. The ether was evaporated off, and the solid residue washed with dilute hydrochloric acid. The residue went into solution in dilute sodium hydroxide, and was precipitated at once, as a flocculent mass, on addition of acid. It crystallized from alcohol in fine needles, which melted at 194°–195°, and acted in every way like the fusible anilide. From the wash-water, on evaporation, there was obtained about an equal quantity of crystals of the infusible anilide, melting at 250°–270°, with decomposition. The experiment was repeated, and the flask kept in a freezing mixture, but with the same result.

1 gram of the chloride was treated with aniline in the presence of water and the same substances obtained, in apparently the same proportions. The only explanation of this seems to be that, in the presence of aniline, there is a partial transformation of the low-melting into the high-melting chloride, as the product used could not have contained more than the meerest trace of the high-melting chloride. Further evidence of a transformation is presented under the action of ammonia.

IX. Action of Ammonia.

1. *Action on the High-Melting Chloride.*—Remsen and Saunders[1] showed that when ammonia acts on the high-melting chloride it is converted into the ammonium salt of saccharin. The following experiments confirm their results and show that nothing else is formed:

3 grams of the chloride was dissolved in ether, cooled to 0° by adding ice, and shaken for some time with very dilute ammonia. The ether solution was dried over calcium chloride and the ether evaporated. From this 2.6 grams of the chloride was recovered unchanged. The water, when evaporated, gave crystals of ammonium chloride, and also of the ammonium salt of saccharin. When acidified it gave a small precipitate

[1] *Loc. cit.*

of saccharin. This experiment was repeated and the ammonia made much more concentrated. Very little of the chloride was recovered from the ether, but from the water, on evaporation, crystals were obtained as above and in large quantity. These had a sweet taste, and when dissolved in water and acid added, there was a copious precipitate of saccharin. There was no evidence of any other substance.

2. *Action on the Low-Melting Chloride.*—The work of Remsen and Saunders, and also that of Mr. A. D. Chambers, of this laboratory, made it extremely probable that when ammonia acts on the low-melting chloride at low temperatures, the ammonium salt of orthocyanbenzenesulphonic acid, $C_6H_4 \begin{matrix} CN \\ SO_2ONH_4 \end{matrix}$, is formed. This substance has been under investigation during this year by Mr. Karslake, of this laboratory.

The following experiments are very interesting in this connection. 0.8 gram of the pure chloride was dissolved in ether, the solution cooled to 0°, and very dilute ammonia added. After shaking for some time, the solution being kept at 0°, the water was drawn off and evaporated nearly to dryness. A few crystals separated, and when these were dissolved in water, and acid added, there was a very small precipitate of saccharin, after a time. The ether solution was dried with calcium chloride, and evaporated nearly to dryness. From this crystals were obtained which resembled the high-melting chloride, melting at 75°–78°, and when heated with water they gave off hydrochloric acid.

The experiment was repeated with 2 grams of the chloride. When the ammonia solution was drawn off, a rapid current of air was passed through it to expel any ether; it was then filtered, evaporated to a small volume, and allowed to stand over night. The next morning there was a good deposit of botryoidal crystals, similar in every way to those obtained by Mr. Chambers, and by Mr. Karslake.

The ether solution was dried with calcium chloride and evaporated. From this was obtained 0.54 gram of the pure high-melting chloride (melting-point 79°–80° uncorr.). These experiments seem to prove that, in the presence of ammonia, the

low-melting is partially changed into the high-melting chloride, as the latter was actually obtained and recognized. This transformation also accounts for the small amount of saccharin obtained in the first experiment, as the high-melting chloride is slowly acted upon by very dilute ammonia. The difference between this case and that of the action of aniline is, that aniline acts readily on both chlorides, and hence the formation of both the fusible and infusible anilides from the low-melting chloride.

X. Action of Benzene and Aluminium Chloride.

1. *Action on the High-Melting Chloride.*—Remsen and Saunders[1] showed that when benzene and aluminium chloride act on the high-melting or mixed chlorides, at ordinary temperatures, orthobenzoylbenzenesulphone chloride is formed, and that when the action is continued at higher temperatures orthobenzoyldiphenylsulphone is formed. Their work was repeated in both cases, and, under the same conditions, both of the substances just mentioned were obtained and recognized by their descriptions. Moreover, the yields were unsatfactory just as they had observed.

2. *Action on the Low-Melting Chloride.*—3 grams of the chloride was dissolved in about 15 grams of benzene, and 3–4 grams of aluminium chloride added in portions. Reaction took place at once, and was so vigorous that the vessel had to be plunged into cold water to prevent too violent action. In about ten minutes action ceased, but on heating momentarily in a water-bath, at about 60°, action began again. This was repeated at intervals for about fifteen minutes, when all action seemed to be over, and a dark-colored heavy layer had separated at the bottom. The whole was then poured into warm water containing a little hydrochloric acid. In a short time a yellowish, oily layer separated at the bottom of the dish, and, when the water was poured off, this soon solidified. It was ground up in a mortar, and, when washed and dried, weighed 3.6 grams. Some of this was crystallized from alcohol and melted at 181°–183°, but on recrystallization it melted at 182°–184° uncorr. In every way it agreed with orthoben-

[1] *Loc. cit.*

zoyldiphenylsulphone. In the mass there was also a little orthobenzoylbenzenesulphone chloride, as was shown by extracting with ether and crystallizing. The reaction went on very smoothly and was more satisfactory than in the case of the high-melting chloride.

The experiment was repeated with 2 grams of the chloride, and the temperature kept down to the freezing-point of benzene. The action was not so vigorous as before, and when it was over the benzene solution was poured into cold water. Instead of evaporating from the water, the benzene layer was poured off and quickly evaporated from a watch-glass. A gummy substance remained, but on washing with alcohol, all the gum was very easily dissolved. The residue, when crystallized from alcohol, melted at 183°–185° uncorr. It was hoped that from the low-melting chloride a substance isomeric with orthobenzoyldiphenylsulphone might be obtained, but there was not the slightest indication of such a substance.

XI. Other Attempts to Effect a Transformation.

1. *By Heat.*—It was hoped that by heating the low-melting chloride it might be possible to change it into the high-melting form. Accordingly, two portions were heated in sealed tubes, the first for seven hours at about 80°, and the second for twelve hours at about 90°. Each of these was then dissolved in ligroin, and recrystallized, but only crystals of the low-melting chloride could be obtained.

2. *By the Action of Water.*—A portion of the low-melting chloride was shaken in a large test-tube with water for about one-half hour, then dried, dissolved in ligroin, and crystallized, but there was no evidence of crystals of the high-melting chloride.

XII. Conclusion.

The results of this investigation may be summed up thus:

1. It has been shown that both the chlorides may be obtained in quantity in pure condition.

2. That water and other agents act on the low-melting chloride much more easily than on the high-melting.

3. That phenol gives two products with each of the chlorides: the diphenyl ether $C_6H_4 \begin{matrix} \diagup CO.OC_6H_5 \\ \diagdown SO_2OC_6H_5 \end{matrix}$, and the chlor-

phenyl ether, $C_6H_4 \begin{cases} CO.OC_6H_5 \\ SO_2Cl \end{cases}$, but no isomeric product.

4. That the diphenyl ether can be decomposed with various agents, but no difference was found in the relations of the two phenol residues to the rest of the compound.

5. That resorcin gives a sulphon fluoresceïn with both chlorides.

6. That with aniline the high-melting chloride gives only the fusible anilide, but the low-melting chloride gives both fusible and infusible anilides; this is accounted for by a partial transformation of the low-melting into the high-melting chloride.

7. That ammonia gives only the ammonium salt if saccharin with the high-melting chloride, but the low-melting chloride is partly transformed into the high-melting form, and partly acts with ammonia to form ammonium orthocyanbenzenesulphonate $C_6H_4 \begin{cases} CN \\ SO_2ONH_4 \end{cases}$.

8. That benzene and aluminium chloride give the same products with both of the chlorides.

Biographical.

The author was born in Mecklenburg County, N. C., August 25, 1864. His early education was received in the public schools, and at Fort Mill Academy (S. C.). In 1884 he entered Davidson College, N. C., from which, in 1888, he received the degree of Bachelor of Arts. From 1888 to 1892 he was an instructor in Bingham School, N. C. In 1892 he entered Johns Hopkins University, where, for the past 3 years, he has pursued courses in chemistry, mineralogy and physics.